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(54) **USE OF TYPE V ADSORBENT AND GAS CONCENTRATION FOR CO2 ADSORPTION AND CAPTURE**

VERWENDUNG VON ADSORBENS DES TYPUS V UND GASKONZENTRATION FÜR CO2-ADSORPTION UND -ABSCHIEDUNG

UTILISATION D'ADSORBANT DE TYPE V ET DE CONCENTRATION DE GAZ POUR L'ADSORPTION ET LA CAPTURE DE CO2

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(56) References cited:
EP-A1- 2 210 656 WO-A1-2017/053062
JP-A- H0 699 035 US-A1- 2017 087 531

- **TIMOTHY C. MERKEL ET AL:** "Selective Exhaust Gas Recycle with Membranes for CO 2 Capture from Natural Gas Combined Cycle Power Plants", **INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH**, vol. 52, no. 3, 23 January 2013 (2013-01-23), pages 1150 - 1159, XP055500754, ISSN: 0888-5885, DOI: 10.1021/ie302110z
- **THOMAS M. MCDONALD ET AL:** "Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-Appended Metal-Organic Framework mmen-Mg 2 (dobpdc)", **JOURNAL OF THE AMERICAN CHEMICAL SOCIETY**, vol. 134, no. 16, 25 April 2012 (2012-04-25), pages 7056 - 7065, XP055065877, ISSN: 0002-7863, DOI: 10.1021/ja300034j
- **THOMAS M. MCDONALD ET AL:** "Cooperative insertion of CO2 in diamine- appended metal-organic frameworks", **NATURE**, vol. 519, no. 7543, 11 March 2015 (2015-03-11), GB, pages 303 - 308, XP055233083, ISSN: 0028-0836, DOI: 10.1038/nature14327

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- **PHILLIP J. MILNER ET AL: "A Diaminopropane-Appended Metal-Organic Framework Enabling Efficient CO₂ Capture from Coal Flue Gas via a Mixed Adsorption Mechanism", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 139, no. 38, 27 September 2017 (2017-09-27), US, pages 13541 - 13553, XP055500671, ISSN: 0002-7863, DOI: 10.1021/jacs.7b07612**

Description

FIELD

[0001] A method is provided for adsorbing CO₂ through the use of Type V adsorbents.

BACKGROUND

[0002] Gas separation is important in many industries and can typically be accomplished by flowing a mixture of gases over an adsorbent that preferentially adsorbs a more readily adsorbed component relative to a less readily adsorbed component of the mixture. One of the more important types of gas separation technology is swing adsorption, such as pressure swing adsorption (PSA). PSA processes rely on the fact that under pressure gases tend to be adsorbed within the pore structure of the microporous adsorbent materials or within the free volume of a polymeric material. The higher the pressure, the greater the amount of targeted gas component will be adsorbed. When the pressure is reduced, the adsorbed targeted component is released, or desorbed. PSA processes can be used to separate gases of a gas mixture because different gases tend to fill the micropore or free volume of the adsorbent to different extents.

[0003] Another important gas separation technique is temperature swing adsorption (TSA). TSA processes also rely on the fact that gases tend to be adsorbed within the pore structure of the microporous adsorbent materials or within the free volume of a polymeric material. When the temperature of the adsorbent is increased, the adsorbed gas is released, or desorbed. By cyclically swinging the temperature of adsorbent beds, TSA processes can be used to separate gases in a mixture when used with an adsorbent that is selective for one or more of the components in a gas mixture.

[0004] Conventional temperature swing adsorption (TSA) processes use a solid adsorbent for the selective adsorption of a desired gas component at a lower temperature followed by desorption of the component at higher temperature. A conventional solid adsorbent can correspond to a monolith type structure or to a bed of solid adsorbent particles.

[0005] Metal organic frameworks (MOFs), especially MOFs exhibiting a Type V isotherm profile, e.g. diamine appended MOFs such as 2,2-dimethyl-1,3-diaminopropane (dmpn) appended to Mg₂(dobpdc) (dobpdc = 4,4'-dioxido-3,3'-biphenyldicarboxylate) and *N,N'*-dimethylethylenediamine (mmen) appended to Mg₂(dobpdc), have shown greatly improved working capacity and energy efficiency (i.e. low temperature of adsorption/desorption) in the adsorption of gases over known adsorbents in the prior art. One cannot take advantage of said improved capacities at low partial pressures of the sorbate gas, e.g. natural gas flue gas where CO₂ concentration is about 3-5%. This translates into low capture recovery performance. It would be advantageous to alter

the concentration of the sorbate to exactly match the optimal capture properties of the adsorbent in highly energy efficient adsorbents such as Type V adsorbents.

[0006] All post-combustion ("PC") CO₂ capture technologies suffer from the disadvantage that the CO₂ in the flue gas is present at low pressure (just about 1 atm) and in low concentrations (3 to 15%). A large amount of energy is needed to separate the CO₂. For 90% recovery of 10% CO₂ in a flue gas at 1 atm, the CO₂ must be brought from 0.1 atm to 1 atm, and then further compressed to a delivery pressure of 150 atm. Analyses conducted at NETL shows that CO₂ capture and compression using a conventional absorption process raises the cost of electricity from a newly built supercritical PC power plant by 86%, from 64 cents/kWh to 118.8 cents/kWh (Julianne M. Klara, DOE/NETL-2007/1281, Revision 1, August 2007, Exhibit 4-48 LCOE for PC Cases). Aqueous amines are considered a state-of-the-art technology for CO₂ capture for PC power plants, but have a cost of \$68/ton of CO₂ avoided) (Klara 2007, DOE/NETL-2007/1282). Developing methods that minimize the amount of energy and other costs will be necessary if CO₂ removal from flue gas is to be economical.

[0007] McDonald et al., J. Am. Chem. Soc. 2012 (134) 7056-7065; McDonale et al., Nature 2015 (519), 303-308; and US Patent Application publication US 2017/0087531 describe the capture of carbon dioxide using the type V adsorbents comprising functionalized metal-organic frameworks.

[0008] Methods for the removal of CO₂ from gas streams, include sorption with a solvent, adsorption with a sorbent, membrane separation, and cryogenic fractionation and combinations thereof. In sorption/desorption processes to capture CO₂, the energy needed to regenerate the sorbent or solvent is a large cost element.

SUMMARY

[0009] Provided is a method for adsorbing CO₂ according to claim 1.

BRIEF DESCRIPTION OF THE FIGURES

[0010]

FIG. 1 schematically shows an example of adsorption isotherms of a gas by Types I-V adsorbents.

FIG. 2 schematically shows an example of adsorption isotherms and potential working capacity for adsorption of CO₂ by a Type I adsorbent.

FIG. 3 schematically shows an example of adsorption isotherms and potential working capacity for adsorption of CO₂ by a Type V adsorbent.

FIGS. 4A & 4B schematically show an example of adsorption isotherms and potential working capacity for adsorption of CO₂ by a Type V adsorbent at an inadequate CO₂ concentration and preferred CO₂ concentration, respectively.

FIG. 5 schematically shows an example of a system suitable for performing a swing adsorption process described herein.

FIGS. 6A & 6B schematically show an example of breakthrough and bypass of CO₂ by a Type V adsorbent at 10% CO₂ feed concentration and an adsorption temperature of 40°C and 75°C, respectively.

FIGS. 7A & 7B schematically show adsorption isotherms for adsorption of CO₂ at 75°C at a CO₂ concentration of 4% and 15%, respectively.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Definitions

[0011] As used herein, the term "breakthrough" refers to the point at which an effluent sorbate concentration is substantially equal to an influent sorbate concentration after exposure to an adsorption bed, which is caused by the adsorption bed being saturated with the sorbate.

[0012] As used herein, the term "bypass" refers to the point at which an increase in an effluent sorbate concentration is seen due to the adsorption isotherm for the particular adsorbent being inactive for sorbate adsorption at a given partial pressure of sorbate in the influent feedstream.

[0013] As used herein, "lower level capture limit" refers to the partial pressure or concentration of sorbate in an influent feedstream below which bypass occurs for a given adsorption isotherm.

Overview

[0014] Swing adsorption processes can have an adsorption step in which a feed mixture (typically in the gas phase) is flowed over and/or exposed to an adsorbent that can preferentially adsorb a more readily adsorbed component relative to a less readily adsorbed component. A component may be more readily adsorbed because of kinetic or equilibrium properties of the adsorbent. The adsorbent is typically contained in a contactor that is part of the swing adsorption unit. In this discussion, a contactor can contain a particulate adsorbent bed, or alternatively the particulate adsorbent can be suspended in a heat transfer fluid to form a slurry. Other components in the swing adsorption unit can be valves, piping, tanks, and other contactors. In some aspects, a plurality of contactors can be used as part of a swing adsorption system. This can allow adsorption and desorption to be performed as a continuous process, with one or more contactors being used for adsorption while one or more additional contactors are used for desorption. As contactors approach maximum loading during adsorption and/or approach complete desorption under the desorption conditions, the flows to the contactors can be switched between adsorption and desorption. It is noted that after the desorption step, the adsorbent may retain a substan-

tial loading of the gas component. In various aspects, the loading of the adsorbent with the adsorbed gas component at the end of the desorption step can be at least about 0.001 mol/kg, or at least about 0.01 mol/kg, or at least about 0.1 mol/kg, or at least about 0.2 mol/kg, or at least about 0.5 mol/kg, or at least about 1.0 mol/kg, and/or about 3.0 mol/kg or less, or about 2.5 mol/kg or less, or about 2.0 mol/kg or less, or about 1.5 mol/kg or less, or about 1.0 mol/kg or less, or about 0.1 mol/kg or less. Additionally or alternately, the loading at the end of the desorption step can be characterized relative to the loading at the end of the prior adsorption step. The loading of the adsorbent with the adsorbed gas component at the end of the desorption step can be at least about 0.01% of the adsorbent loading at the end of the prior adsorption step, or at least about 0.1%, or at least about 1%, or at least about 5%, or at least about 10%, or at least about 20%, or at least about 30%, or at least about 50%, and/or about 90% or less, or about 70% or less, or about 50% or less, or about 40% or less, or about 30% or less, or about 20% or less, or about 10% or less, or about 5% or less, or about 1% or less, or about 0.1% or less.

[0015] The method of adsorbent regeneration designates the type of swing adsorption process. Pressure swing adsorption (PSA) processes rely on the fact that gases under pressure tend to be adsorbed within the pore structure of the microporous adsorbent materials. The higher the pressure, the greater the amount of targeted gas component that will be adsorbed. When the pressure is reduced, the adsorbed targeted component is released, or desorbed. PSA processes can be used to separate gases of a gas mixture because different gases tend to fill the micropore or free volume of the adsorbent to different extents due to either the equilibrium or kinetic properties of the adsorbent. Temperature swing adsorption (TSA) processes also rely on the fact that gases tend to be adsorbed within the pore structure of the microporous adsorbent materials. When the temperature of the adsorbent is increased, the adsorbed gas is released, or desorbed. By cyclically swinging the temperature of adsorbent beds, TSA processes can be used to separate gases in a mixture when used with an adsorbent that is selective for one or more of the components in a gas mixture.

[0016] Temperature swing adsorption (TSA) processes, also referred to as thermal swing adsorption processes, can employ an adsorbent that is repeatedly cycled through at least two steps - an adsorption step and a thermally assisted regeneration step. Regeneration of the adsorbent can be achieved by heating the adsorbent to an effective temperature to desorb target components from the adsorbent. The adsorbent can then be cooled so that another adsorption step can be completed. The cycle time between successive adsorption steps for TSA process can typically be on the order of minutes, such as from about 0.2 minutes to about 120 minutes or more. In some aspects, the cycle time between successive adsorption steps for a TSA process can be less than about

30 minutes, or less than about 10 minutes, or less than about 2 minutes, or less than about 1 minute. The cycle time can depend in part on the nature of the adsorbent bed, such as the depth of the bed for a trickle bed contactor. TSA processes can be used to obtain very high product recoveries in the excess of 90 vol %, for example greater than 95 vol % or, in some cases, greater than 98 vol %. The term "adsorption" as used herein includes physisorption, chemisorption, and condensation onto a solid support, absorption into a solid supported liquid, chemisorption into a solid supported liquid, and combinations thereof.

[0017] A TSA cycle can also typically include a change in the temperature of the adsorbent from the temperature for the adsorption step to the temperature for the desorption step. The adsorption step can be defined based on the time when the gas flow is started for the input gas containing the component for adsorption and when the gas flow is stopped. The desorption step can be defined based on the time when gas being desorbed from the adsorbent is collected to the time collection is stopped. Any time in the cycle outside of those steps can be used for additional adjustment of the adsorbent temperature. In some aspects, a heat transfer fluid can allow a TSA cycle to be performed that corresponds to only the adsorption step and the desorption step, as the heat transfer fluid can allow an adsorption / desorption step to be started without necessarily requiring an intervening step to adjust the temperature of the bed.

[0018] A potential advantage of a TSA separation can be that the process can be performed at a convenient pressure, or with a small amount of variation around a convenient pressure. For example, a goal of a TSA separation can be to develop a substantially pure stream of a gas component that is adsorbed and then desorbed. In this type of aspect, a convenient pressure for the desorption step can be a pressure of about 1 bar (100 kPa) or less. Attempting to desorb a stream at greater than about 100 kPa can require substantial additional temperature increase for desorption. Additionally, ambient pressure can be a convenient pressure for the adsorption step as well, as many streams containing a gas component for adsorption can correspond to "waste" or flue gas streams that may be at low pressure. In some aspects, the pressure difference between the adsorption and desorption steps can be about 1,000 kPa or less, or about 200 kPa or less, or about 100 kPa or less, or about 50 kPa or less, or about 10 kPa or less.

[0019] A variety of types of solid adsorbents are available for separation of components from a gas flow using temperature swing adsorption (TSA). During a conventional TSA process, at least one component in a gas flow can be preferentially adsorbed by the solid adsorbent, resulting in a stream with a reduced concentration of the adsorbed component. The adsorbed component can then be desorbed and/or displaced from the solid adsorbent, optionally to form a stream having an increased concentration of the adsorbed component.

[0020] In this description, reference is made at various locations to adsorbing CO₂ from a gas feed and subsequently desorbing a substantially pure CO₂ stream.

In this example, a flue gas from a refinery process or a gas power plant can have a CO₂ concentration of about 0.1 vol% to about 10 vol%. It would be desirable to be able to adsorb CO₂ from the flue gas stream and then desorb the CO₂ to form a concentrated CO₂ stream, such as a stream having at least 90 vol% CO₂, or at least 95 vol%, or at least 98 vol%. The amount of CO₂ that can be adsorbed and then desorbed as part of an adsorption / desorption cycle is referred to as a working capacity for the adsorbent with respect to CO₂ / the gas component.

15 Type V Isotherm Adsorbents

[0021] Adsorbents can be characterized based on the type of adsorption isotherm the adsorbent has for a given gas component. Adsorbents can generally be classified into six types based on the 1985 IUPAC classification of adsorption isotherms. Type I adsorbents have adsorption isotherms that correspond to monolayer adsorption of a gas component and that can generally be represented by a Langmuir Adsorption Isotherm. For a Type I isotherm, a monolayer can be readily adsorbed, with little or no additional adsorption beyond a monolayer as pressure increases. Type II adsorbents have adsorption isotherms corresponding to multi-layer adsorption, with a plateau at intermediate pressures corresponding to monolayer adsorption. Type III adsorbents exhibit multi-layer adsorption without an intermediate plateau corresponding to monolayer adsorption. Type IV and Type V adsorbents are similar to Type II and Type III adsorbents, respectively, but correspond to adsorbents having micropores and/or mesopores that can allow for capillary condensation. This can result in hysteresis in adsorbent behavior. Type VI isotherms represent a stepwise adsorption process, in which successive two-dimensional phase transitions may take place. It is noted that some adsorbents may not have "isotherms" for adsorption under the strict definition of an isotherm. This can be due, for example, to structural and/or phase changes that occur in the adsorbent as the temperature changes. In this discussion, adsorbents are defined as Type I - Type VI adsorbents based on the corresponding IUPAC classification, even if the shape of the adsorption profile does not represent a true "isotherm" due to changes in the adsorbent structure during adsorption. Figure 1 provides schematic representations of typical adsorption isotherms for Types I-V.

[0022] The method provided herein adjust the concentration of a CO₂ within an input fluid to optimize the capture properties of highly Type V adsorbents. Because of the stepwise nature of the Type V isotherms, the working capacity for adsorbents like mmen-Mg₂(dobpdc) and dmpn-Mg₂(dobpdc) can be similar to the total adsorption capacity, such as at least about 80% of the total capacity at the adsorption conditions, or at least about 90% of the

total capacity. This is in contrast to the working capacity for many typical adsorbents having Type I isotherms, where the working capacity is less than about 1 mol/kg and/or the working capacity corresponds to less than about 50% of the total adsorbent capacity at the adsorption conditions.

[0023] FIG. 2 shows an example of CO₂ adsorption isotherms for zeolite 13X, which exhibits a Type I adsorption isotherm. It is noted that use of zeolite 13X for adsorption / desorption of CO₂ can pose some difficulties due to the presence of H₂O in typical flue gases. However, zeolite 13X is suitable for illustrating the concepts of an adsorption / desorption cycle. In FIG. 2, a CO₂ concentration of 4 vol% was selected as a representative dilute concentration for CO₂, such as a concentration of CO₂ that might occur in a flue gas. In FIG. 2, the vertical dotted lines show the partial pressure of CO₂ (at 4 kPa or 100 kPa) that corresponds to a concentration of either 4 vol% or 100 vol%. As shown in FIG. 2, the adsorption isotherm changes with temperature, with lower temperatures corresponding to higher amounts of adsorbed CO₂ at a given temperature.

[0024] One method for determining a working capacity is based on adsorption isotherms for a gas component / solid adsorbent combination. Using the adsorption isotherms, and based on an expected concentration of the gas component during adsorption and desorption, the working capacity can be calculated as the difference in the adsorbed amount of the gas component under the adsorption and desorption conditions. The values shown in FIG. 2 can allow for determination of a working capacity for CO₂ adsorption by zeolite 13X at an adsorption temperature of 27°C and a desorption temperature of 140°C. Based on the values of FIG. 2, at a total pressure of about 100 kPa, the working capacity of the adsorbent is about 0.5 moles CO₂ per kilogram of adsorbent, as shown by the horizontal lines in FIG. 2. The intersection of the 27°C isotherm and the dotted vertical line corresponding to 4 vol% CO₂ represents the adsorption capacity of the adsorbent for adsorption of CO₂ from a gas stream during a hypothetical adsorption step at 100 kPa and 27°C, which is about 3 mol CO₂/kg. Similarly, the intersection of the 140°C isotherm and the dotted vertical line corresponding to 100% CO₂ represents the expected amount of CO₂ retained by the adsorbent when attempting to desorb a substantially pure CO₂ stream at 140°C and 100 kPa, which is about 2.5 mol CO₂/kg. The horizontal lines in FIG. 2 illustrate the difference in these values, corresponding to the working capacity of about 0.5 mol CO₂/kg.

[0025] The above calculation of a working capacity based on the 27°C isotherm and the 140°C isotherm represents an idealized value for the working capacity. Unfortunately, real working capacities for adsorbents are typically lower than the idealized value due to temperature increases in an adsorbent during the adsorption portion of a cycle. When a gas component is adsorbed by a solid adsorbent, an amount of heat corresponding to a

heat of adsorption can be generated. This generated heat typically leads to an increase in the temperature of the adsorbent, due in part to the limited heat capacity of a gas flow to transport heat away from the adsorbent. For an adsorption amount roughly corresponding to a mole per kilogram, the corresponding temperature increase of the adsorbent can be on the order of tens of degrees Celsius. FIG. 2 shows an example of how this increase in the temperature of the adsorbent can impact the working capacity. For the example shown in FIG. 2, an increase in the adsorbent temperature from 27°C to 45°C (a representative temperature increase which could occur based on adsorption of a gas component by an adsorbent) can shift the isotherm. At 45°C the working capacity of the adsorbent would be reduced even further, e.g., to about 0 moles per kilogram assuming a desorption temperature of 140°C.

[0026] For a classical Type I adsorbent the steepness of the isotherm gradually diminishes as the temperature increases (as shown in FIG. 2), necessitating a high desorption temperature to achieve a large working capacity for a separation. In contrast, in Type V adsorbent isotherms, the position of the isotherm step shifts markedly to higher pressures as the temperature increases, such that a large working capacity can be achieved with only a small increase in temperature. For an efficient carbon capture process with high CO₂ recovery (i.e. high CO₂ removal from the flue gas) and high CO₂ purity in the product stream, one would ideally create a Type V adsorbent with a large vertical step positioned below the partial pressure of CO₂ in the flue gas needed to achieve the desired CO₂ recovery, i.e. at the lower level capture limit of the adsorbent.

[0027] Type V isotherm adsorbents have great potential as high working capacity adsorbents but suffer from low capture rates at low partial pressures. That is, an adsorbent with a Type V adsorption step to capture ≥90% of the CO₂ from a natural gas power plant flue gas of 4% CO₂ is challenging because the adsorbent would have to capture CO₂ down to ≤0.4% while having a desorption temperature lower than the temperature at which the appended diamine starts to be lost due to volatilization or degradation. Indeed capture at the lower CO₂ partial pressures goes in hand with high desorption temperatures. Thus, the input sorbate's partial pressure and the gas temperature during adsorption become critical parameters for process design. Temperature can be varied but temperatures approaching and below room temperature become cost prohibitive.

[0028] FIG. 3 shows an example of CO₂ isotherms (calculated using an empirical model) for a material that is a Type V adsorbent for CO₂. The modeled material in FIG. 3 is mmen-Mg₂(dobpdc). This material has an expanded MOF-74 structure, with the mmen being a diamine functionalization of the 18.4 Angstrom channels in the structure. Additional details regarding the material can be found, for example, in mmen-Mg₂(dobpdc) adsorbent, Thomas M. McDonald, Woo Ram Lee, Jarad A. Mason,

Brian M. Wiers, Chang Seop Hong, and Jeffrey R. Long, *J. Am. Chem. Soc.* 2012, 134, 7056-7065. FIG. 3 models CO₂ adsorption of a feedstream with 4% CO₂ with a desired CO₂ reduction of 90%, i.e., a reduction to 0.4% CO₂. As shown this CO₂ reduction goal can be achieved at an adsorption temperature of 50°C and a desorption temperature of 155°C.

[0029] FIGS. 4A and 4B show an example of CO₂ isotherms for a material that is a Type V adsorbent for CO₂ at differing levels of CO₂ in the feedstream. The material in FIGS. 4A and 4B is dmpn-Mg₂(dobpdc) (Milner, Phillip J., et al., "A Diaminopropane-Appended Metal-Organic Framework Enabling Efficient CO₂ Capture from Coal Flue Gas Via a Mixed Adsorption Mechanism", *Journal of the American Chemical Society*, 2017, 139, 13541-13553). FIG. 4A illustrates the case where there is insufficient CO₂ concentration in the feed to effectively take advantage of the Type V adsorbent's working capacity and avoid bypass of CO₂ through the adsorbent. The dashed line on the isotherm illustrates adsorption of a natural gas power plant flue gas, which has a CO₂ concentration of about 4% (40 mbar). In order to decrease the CO₂ concentration by 90%, the isotherm should show sufficient adsorption at a CO₂ concentration of about 0.4% (4 mbar) defined by the dotted line. Using an adsorption temperature of 40°C and a desorption temperature of 100°C, we see in FIG. 4A that at 0.4% CO₂, there is negligible adsorption (-0.08 mol/kg), which means that a significant amount of CO₂ is bypassing the adsorbent entirely. Lowering the temperature of the flue gas could shift the isotherm to the left on the plot, but lowering an adsorption temperature below 40°C becomes prohibitively expensive in refinery and power plant conditions. A better option, which is disclosed herein is to shift the operating window by increasing the partial pressure of CO₂ in the feedstream-i.e. increase the CO₂ concentration of a natural gas power plant flue gas to more closely mimic the CO₂ concentration of a coal power plant flue gas.

[0030] FIG. 4B practically illustrates the advantage of including a CO₂ concentrator in the process to effectively take advantage of the Type V adsorption isotherm profile. The isotherm shown in 4B relates to a feedstream that has been concentrated to -15% or -150 mbar CO₂ with an adsorption temperature of 40°C, a desorption temperature of 100°C, and a CO₂ reduction of at least 90% to -1.5% or -15 mbar. Thus, in order to achieve this reduction goal at the specified temperatures, one would want an adsorbent displaying a step change at approximately 15 mbar or lower, which FIG. 4B clearly shows (step change, or lower level capture limit, occurring at about 10 mbar). At the 1.5% CO₂ level, CO₂ is still being adsorbed at about 0.45 mol/kg.

[0031] Described herein but not claimed is a gas concentrator to increase the concentration of a sorbate gas to a level to optimize the adsorption characteristics of the high capacity adsorbent. Post combustion concentration of CO₂ in natural gas flue gas is known in the art and can

be accomplished in a number of different ways. For example, U.S. Publication No. 2017/0087503 to Sundaram describes a two-stage adsorbent and process whereby a first TSA adsorption process is used as a CO₂ concentrator to form a CO₂ rich stream to be further separated in a second stage adsorption process. Sundaram describes a number of adsorbent contactors to be used in the process such as parallel plate contactors, adsorbent monoliths, and metal organic frameworks. In a publication by Merkel, T.C. et al., *Selective Exhaust Gas Recycle with Membranes for CO₂ Capture from Natural Gas Combined Cycle Power Plants*, 52 *INDUS. & ENG'G CHEM. RES.* 1150-59 (2013), the authors describe exhaust gas recycle processes whereby natural gas flue gas is contacted with a membrane selective for CO₂ over O₂ and N₂ to create a CO₂-enriched permeate stream.

[0032] Additionally, CO₂ concentration in an exhaust stream can be enriched prior to combustion by providing an oxidant enriched in O₂. For example, if the fuel is methane and the oxidant is air, then exhaust stream has a CO₂ concentration of about 4%. One could enrich the air with oxygen, thereby increasing the exhaust CO₂ concentration.

[0033] Another necessary aspect in working with Type V adsorbents is heat management. Natural gas power plant flue gas typically needs to be cooled prior to contact with an adsorbent bed-the flue gas typically exits a heat recovery steam generator at about 120°C. As shown in FIG. 3 when used as an adsorbent for a sorbate gas, Type V adsorbents can be highly sensitive to temperature increases. For process control, it can be desirable to cool the flue gas to an initial adsorption temperature that is greater than ambient, so that the adsorption process is repeatable independent of ambient conditions and water co-adsorption is lower at higher temperatures which also leads to lower parasitic energy.

[0034] Additionally, heat is generated during the adsorption process. The heat generated during CO₂ adsorption of the about 3 mol/kg capacity of the adsorbent can increase the temperature of the adsorbent by about 50°C or more. Under conventional conditions, this can lead to low actual working capacity and/or unpredictable working capacity. In the case of a Type V adsorbent such as mmen-Mg₂(dobpdc) such a temperature increase would allow CO₂ bypass. Thus, it can be beneficial to deploy cooling to the adsorbent bed itself. Using a cooler, the temperature increase during adsorption of CO₂ can be reduced or minimized, so that the temperature increase for the adsorbent should be less than the amount needed to keep the adsorption operating above the lower level capture limit, and such a temperature increase can be 25°C or less, 20°C or less, 15°C or less, 10°C or less, or 5°C or less, or 2°C or less. For this type of reduced or minimized temperature increase, an initial adsorption temperature can be selected that allows for adsorption of at least the full stepwise increase in the isotherm.

[0035] Accordingly, a heat management system can reduce the temperature of the flue gas and/or minimize

the temperature increase of the solid adsorbent that occurs during an adsorption cycle. Minimizing such a temperature increase can enhance the working capacity for an adsorbent and/or enable the use of adsorbents (such as Type V adsorbents) that are not practical for commercial scale adsorption using conventional adsorption methods. Example heat managed adsorbers include a trickle bed adsorber, as described in U.S. Publication No. 2017/0087506, hollow fiber contactors, parallel channel monoliths (optionally 3D printed) with alternating gas and liquid channels, and shell/tube heat exchangers with adsorbent. This can allow for heat transfer in combination with using relative liquid/gas velocities in a way that the thermal front moves faster than the adsorption front. This can allow for improved heat recuperation and/or thermal management of the adsorbent. Any loss of adsorption capacity from heat of adsorption can be reduced or minimized, which can make the use of high capacity adsorbents more practical, including (but not limited to) Type V adsorbents. In the case of the trickle bed adsorber, the heat removal is so great that it may not be necessary to cool the incoming natural gas flue gas.

Contactors Configuration

[0036] In various aspects, an improved Type V adsorbent contactor process and system are manipulating the partial pressure of a sorbate gas in a feedstream to maximize adsorption efficiency of the Type V adsorbent and to minimize bypass. FIG. 5 illustrates exemplary Type V contactor system 500. As shown, feedstream 504 containing a sorbate gas (e.g. flue gas from a natural gas power plant containing CO₂) is admitted to cooler 501 so as to bring the temperature of the feedstream to the appropriate adsorption temperature for adsorption in Type V adsorbent 503. The appropriate adsorption temperature will preferably be just above ambient temperatures, e.g. 20-70°C, 30-60°C, 40-50°C. The cooled feedstream is next admitted to concentrator 502, which produces a sorbate-rich stream and a sorbate-lean stream 505. The sorbate-rich stream is then admitted to Type V adsorbent contactor 503. The sorbate-lean stream can be recycled into feedstream 504 or can be routed to other refinery or power plant components for further processing. The sorbate-rich stream should have sufficient concentration of the sorbate gas such that the stepwise increase in the adsorption isotherm occurs below the desired partial pressure of sorbate gas in effluent stream 506. Effluent stream 506 will generally have a partial pressure (or concentration) of sorbate gas that is at least 80%, at least 85%, at least 90%, or at least 95% less than the partial pressure (or concentration) of the sorbate-rich stream. Temperature in the Type V adsorbent contactor 503 can then be raised to the desorption temperature for the adsorbed gas, which then creates desorbed stream 507, which can then be routed for sequestration. The desorption temperature is preferably less than 200°C, less than 175°C, less than 150°C, less than 125°C, or less than

100°C. It should be appreciated that the above parameters may also be stated in ranges, e.g. 80-95% reduction or 100-200°C, and all combinations of the above are contemplated.

[0037] It must be noted that this is merely an exemplary system and the system components can be merged or in different orders. For example, in the case of a trickle bed adsorber, the cooler 501 is incorporated in the Type V adsorbent 503. In the case of O₂ enriched combustion to produce higher concentration of CO₂ in the combustion effluent, the concentrator 502 occurs before the cooler 501.

Examples: Avoiding Bypass

[0038] FIGS. 6A and 6B illustrate the affect that adsorption temperature can have on a Type V isotherm adsorbent. In FIG. 6A, the adsorbent bed is comprised of 209.6 mg mmen-Mg₂(dobpdc) adsorbent mixed with 1g quartz chips to mitigate the temperature increase due to heat of adsorption. The bed was activated by exposure to a dry N₂ flow at 120°C overnight. The feedstream is comprised of 10% CO₂ concentration with the balance N₂. The feedstream is introduced to the bed at a feed rate of 20 sccm (standard cubic centimeter per minute). The adsorption temperature is 40°C and the desorption temperature is 120°C. The graph depicts CO₂ concentration in effluent stream and temperature. As shown, there is no CO₂ in the effluent stream, i.e. no bypass, until about 500 seconds, at which CO₂ concentration jumps to 10% indicating saturation or breakthrough of the adsorbent bed. Temperature is then increased to 120°C to desorb the adsorbed CO₂, the desorption evidenced by the spike in CO₂ concentration occurring at about 1400 seconds.

[0039] FIG. 6B depicts all the same parameters described immediately above with respect to FIG. 6A except that adsorption temperature is raised to 75°C (this is the equivalent of moving the adsorption isotherm depicted in FIG. 3 to the right). In this case, we begin to see CO₂ bypass of about 1.2% between 100 and 200 seconds. This means that at an adsorption temperature of 75°C, no CO₂ is adsorbed below 1.2% CO₂ concentration. Accordingly, a 90% reduction in CO₂ is unachievable with the mmen-Mg₂(dobpdc) adsorbent with a feedstream concentration of less than 12% CO₂ at an adsorption temperature of 75°C.

[0040] This is confirmed by plots 7A and 7B, which show experimental Type V adsorption isotherms for an adsorption temperature of 75°C. Specifically, we see that the stepwise increase in the isotherm, i.e. the lower level capture limit, occurs precisely at 1.2% CO₂ concentration, which corresponds to the point at which bypass is seen in FIG. 6B. Thus, in order to achieve 90% CO₂ adsorption one may employ any number of concentrators described herein to increase the CO₂ concentration of the feedstream to avoid bypass in the adsorbent bed. FIG. 7B shows that concentrating the CO₂ to 15% allows

for a 90% reduction in CO₂ to 1.5% without bypass.

Claims

1. A method for adsorbing CO₂, comprising:

providing a feedstream at a first temperature, the feedstream comprising a first concentration of CO₂;

cooling the feedstream to a second temperature; the second temperature being lower than the first temperature;

exposing the feedstream to a concentrator comprising a membrane, metal organic framework, or a combination thereof, thereby creating an enriched feedstream with a second concentration of CO₂;

the second concentration of CO₂ being higher than the first concentration of CO₂;

exposing the enriched feedstream to adsorbent particles to produce an adsorbent effluent having a lower concentration of CO₂ than the feedstream; wherein the adsorbent particles comprise a Type V adsorbent; and

desorbing at least a portion of CO₂ from the adsorbent particles at a desorption temperature greater than the second temperature, wherein the second concentration of CO₂ is above the lower level capture limit of the Type V adsorbent, wherein the lower level capture limit is the partial pressure of CO₂ in the feedstream below which bypass occurs.

2. The method of claim 1, wherein the feedstream is selected from a combustion flue gas; a natural gas combustion flue gas; and natural gas.

3. The method of any of the previous claims, wherein the first concentration of CO₂ is 1-10 vol%.

4. The method of any of the previous claims, wherein the second concentration of CO₂ is 10-25 vol%.

5. The method any of the previous claims, wherein a loading of adsorbed CO₂ in the adsorbent particles after the desorbing is less than 50% of the loading of CO₂ in the adsorbent particles at the end of the exposing.

6. The method of any of the previous claims, wherein the desorption temperature is greater than the second temperature by at least 20°C.

7. The method of any of the previous claims, wherein the cooling the feedstream comprises cooling the feedstream upstream of the concentrator.

8. The method of any of the previous claims, wherein cooling the feedstream comprises cooling the feedstream concurrently with exposing the enriched feedstream to the adsorbent particles; preferably wherein the cooling is achieved via trickle bed contactor, hollow fiber contactors, parallel channel monoliths with alternating gas and liquid channels, shell/tube heat exchangers, or a combination thereof.

9. The method of any of the previous claims, wherein the feedstream is a post-combustion feedstream and the exposing the feedstream to a concentrator comprises: enriching a pre-combustion feedstream with O₂, and combusting the pre-combustion feedstream to produce the post-combustion feedstream enriched in CO₂.

10. The method of any of the previous claims, wherein the exposing the input fluid to the adsorbent particles comprises exposing the input fluid to the adsorbent particles in a slurry contactor, a fluidized bed contactor, a trickle bed contactor, hollow fiber contactors, parallel channel monoliths with alternating gas and liquid channels, shell/tube heat exchangers, or a combination thereof.

11. The method of any of the previous claims, wherein the adsorbent particles comprise an amine appended metal organic framework; preferably one of N,N'-dimethylethylenediamine appended to Mg₂(4,4'-dioxido-3,3'-biphenyldicarboxylate) (mmen-Mg₂(dobpdc)) and 2,2-dimethyl-1,3-diaminopropane appended to Mg₂(4,4'-dioxido-3,3'-biphenyldicarboxylate) (dmpn-Mg₂(dobpdc)).

Patentansprüche

1. Verfahren zum Absorbieren von CO₂, bei dem

ein Einsatzmaterialstrom bei einer ersten Temperatur bereitgestellt wird, wobei der Einsatzmaterialstrom eine erste Konzentration an CO₂ umfasst,

der Einsatzmaterialstrom auf eine zweite Temperatur gekühlt wird, wobei die zweite Temperatur niedriger als die erste Temperatur ist,

der Einsatzmaterialstrom einer Anreicherungsanlage exponiert wird, die eine Membran, metallorganisches Gerüstmaterial oder eine Kombination davon umfasst, wodurch ein angereicherter Einsatzmaterialstrom mit einer zweiten Konzentration an CO₂ erzeugt wird,

wobei die zweite Konzentration von CO₂ höher als die erste Konzentration von CO₂ ist, der angereicherte Einsatzmaterialstrom gegenüber Adsorbenspartikeln exponiert wird, um ei-

- nen Adsorbensausfluss mit einer niedrigeren Konzentration an CO₂ als der Einsatzmaterialstrom zu produzieren, wobei die Adsorbenspartikel Adsorbens vom Typ V umfassen, und mindestens ein Anteil an CO₂ von den Adsorbenspartikeln bei einer Desorptionstemperatur, die höher als die zweite Temperatur ist, desorbiert wird, wobei die zweite Konzentration an CO₂ über dem unteren Niveau der Einfanggrenze des Adsorbens vom Typ V ist, wobei das untere Niveau der Einfanggrenze der Partialdruck von CO₂ in dem Einsatzmaterialstrom ist, unterhalb dessen Bypass auftritt.
2. Verfahren nach Anspruch 1, bei dem der Einsatzmaterialstrom ausgewählt ist aus einem Verbrennungsabgas, einem Erdgas-Verbrennungsabgas und Erdgas.
 3. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die erste Konzentration an CO₂ 1 bis 10 Vol.% beträgt.
 4. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die zweite Konzentration an CO₂ 10 bis 25 Vol.% beträgt.
 5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem eine Beladung des adsorbierten CO₂ in den Adsorbenspartikeln nach dem Desorbieren weniger als 50 % der Beladung an CO₂ in den Adsorbenspartikeln am Ende der Exposition beträgt
 6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Desorptionstemperatur um mindestens 20°C höher als die zweite Temperatur ist.
 7. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Kühlen des Einsatzmaterialstroms Kühlen des Einsatzmaterialstroms stromaufwärts von der Anreicherungsanlage umfasst.
 8. Verfahren nach einem der vorhergehenden Ansprüche, bei dem Kühlen des Einsatzmaterialstroms Kühlen des Einsatzmaterialstroms gleichzeitig mit dem Exponieren des angereicherten Einsatzmaterialstroms gegenüber den Adsorbenspartikeln umfasst, wobei das Kühlen vorzugsweise mittels Rieselbettkontaktors, Hohlfaserkontaktoren, Parallelkanalmonolithen mit alternierenden Gas- und Flüssigkeitskanälen, Rohrbündelwärmetauschern oder einer Kombination davon erreicht wird.
 9. Verfahren nach einem der vorhergehenden Ansprüche, bei dem der Einsatzmaterialstrom ein Nachverbrennungs-Einsatzmaterialstrom ist und das Exponieren des Einsatzmaterials gegenüber einer Anreicherungsanlage Anreichern eines Vorverbrennungs-Einsatzmaterialstroms mit O₂ und Verbrennen des Vorverbrennungs-Einsatzmaterialstroms umfasst, um den an CO₂ angereicherten Nachverbrennungs-Einsatzmaterialstrom zu produzieren.
 10. Verfahren nach einem der vorhergehenden Ansprüche, bei dem Exponieren des Eingangsfluids gegenüber den Adsorbenspartikeln Exponieren des Eingangsfluids gegenüber den Adsorbenspartikeln in einem Aufschlammungskontaktor, einem Wirbelbettkontaktors, einem Rieselbettkontaktors, Hohlfaserkontaktoren, Parallelkanalmonolithen mit alternierenden Gas- und Flüssigkeitskanälen, Rohrbündelwärmetauschern oder einer Kombination davon umfasst.
 11. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Adsorbenspartikel ein metallorganisches Gerüstmaterial mit angefügtem Amin umfassen, vorzugsweise eines von N,N'-Dimethylethylendiamin angefügt an Mg₂ (4,4'-Dioxido-3,3'-biphenyl-dicarboxylat) (mmen-Mg₂(dobpdc)) und 2,2-Dimethyl-1,3-diaminopropan angefügt an Mg₂(4,4'-Dioxido-3,3'-biphenyldi-carboxylat) (dmpn-Mg₂(dobpdc)) .

Revendications

1. Procédé pour l'adsorption de CO₂, comprenant :

la fourniture d'un flux d'alimentation à une première température, le flux d'alimentation comprenant une première concentration de CO₂ ; le refroidissement du flux d'alimentation jusqu'à une deuxième température ; la deuxième température étant plus basse que la première température ; l'exposition du flux d'alimentation à un dispositif de concentration comprenant une membrane, une structure organique métallique ou une combinaison correspondante, créant ainsi un flux d'alimentation enrichi comportant une deuxième concentration de CO₂ ; la deuxième concentration de CO₂ étant plus élevée que la première concentration de CO₂ ; l'exposition du flux d'alimentation enrichi à des particules d'adsorbant pour produire un effluent d'adsorbant ayant une concentration plus basse de CO₂ que le flux d'alimentation ; les particules d'adsorbant comprenant un adsorbant de type V ; et la désorption d'au moins une partie de CO₂ des particules d'adsorbant à une température de désorption supérieure à la deuxième température, la deuxième concentration de CO₂ étant supérieure à la limite inférieure de capture de l'adsorbant de type V, la limite inférieure de capture

- étant la pression partielle de CO₂ dans le flux d'alimentation en dessous de laquelle une dériviation se produit.
2. Procédé selon la revendication 1, le flux d'alimentation étant choisi parmi un gaz de combustion ; un gaz de combustion de gaz naturel ; et du gaz naturel. 5
 3. Procédé selon l'une quelconque des revendications précédentes, la première concentration de CO₂ étant de 1 à 10 % en volume. 10
 4. Procédé selon l'une quelconque des revendications précédentes, la deuxième concentration de CO₂ étant de 10 à 25 % en volume. 15
 5. Procédé selon l'une quelconque des revendications précédentes, une charge de CO₂ adsorbé dans les particules d'adsorbant après la désorption étant inférieure à 50 % de la charge de CO₂ dans les particules d'adsorbant à la fin de l'exposition. 20
 6. Procédé selon l'une quelconque des revendications précédentes, la température de désorption étant supérieure d'au moins 20 °C à la deuxième température. 25
 7. Procédé selon l'une quelconque des revendications précédentes, le refroidissement du flux d'alimentation comprenant le refroidissement du flux d'alimentation en amont du dispositif de concentration. 30
 8. Procédé selon l'une quelconque des revendications précédentes, le refroidissement du flux d'alimentation comprenant le refroidissement du flux d'alimentation simultanément à l'exposition du flux d'alimentation enrichi aux particules d'adsorbant ; préféra- 35
blement le refroidissement étant réalisé via un contacteur à lit ruisselant, des contacteurs à fibres creuses, des monolithes à canaux parallèles comportant en alternance des canaux pour gaz et pour liquide, des échangeurs de chaleur à enveloppe/tube ou une 40
combinaison correspondante.
 9. Procédé selon l'une quelconque des revendications précédentes, le flux d'alimentation étant un flux d'alimentation post-combustion et l'exposition du flux d'alimentation à un dispositif de concentration comprenant : l'enrichissement d'un flux d'alimenta- 45
tion pré-combustion avec O₂, et la combustion du flux d'alimentation pré-combustion pour produire le flux d'alimentation post-combustion enrichi en CO₂. 50
 10. Procédé selon l'une quelconque des revendications précédentes, l'exposition du fluide d'entrée aux parti- 55
cules d'adsorbant comprenant l'exposition du fluide d'entrée aux particules d'adsorbant dans un contacteur à suspension, un contacteur à lit fluidisé, un con-
tacteur à lit ruisselant, des contacteurs à fibres creuses, des monolithes à canaux parallèles comportant en alternance des canaux pour gaz et pour liquide, des échangeurs de chaleur à enveloppe/tube ou une combinaison correspondante.
 11. Procédé selon l'une quelconque des revendications précédentes, les particules d'adsorbant comprenant une structure organique métallique à amine annexée ; préféra-
blement N,N'-diméthyléthylènediamine annexée à Mg₂(4,4'-dioxydo-3,3'-biphényldicarboxylate) (mmen-Mg₂(dobpdc)) et 2,2-diméthyl-1,3-diaminopropane annexé à Mg₂(4,4'-dioxido-3,3'-biphényldicarboxylate) (dmpn-Mg₂ (dobpdc)).

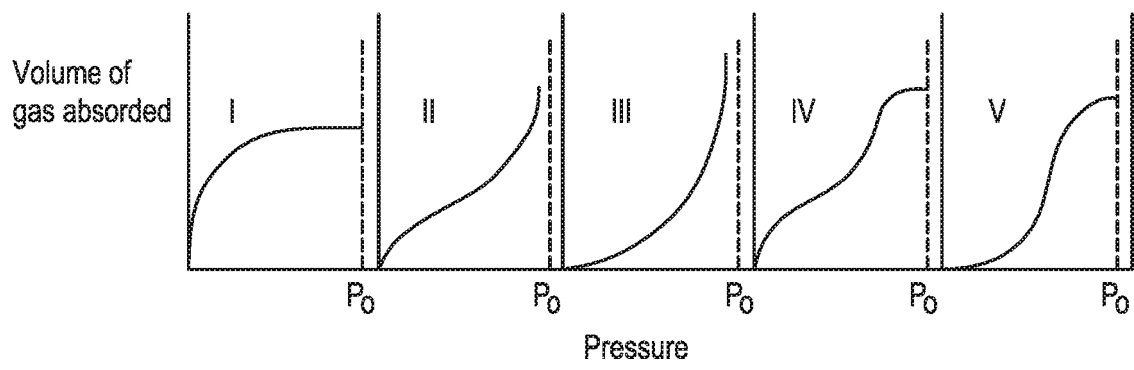


FIG. 1

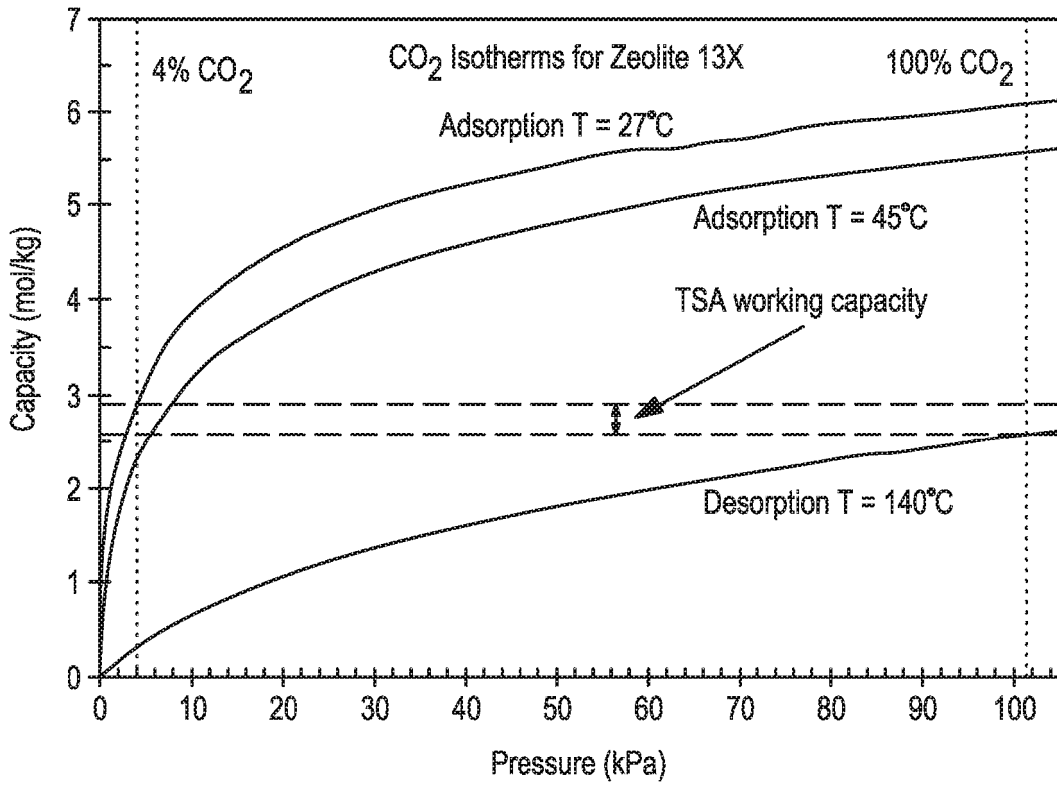


FIG. 2

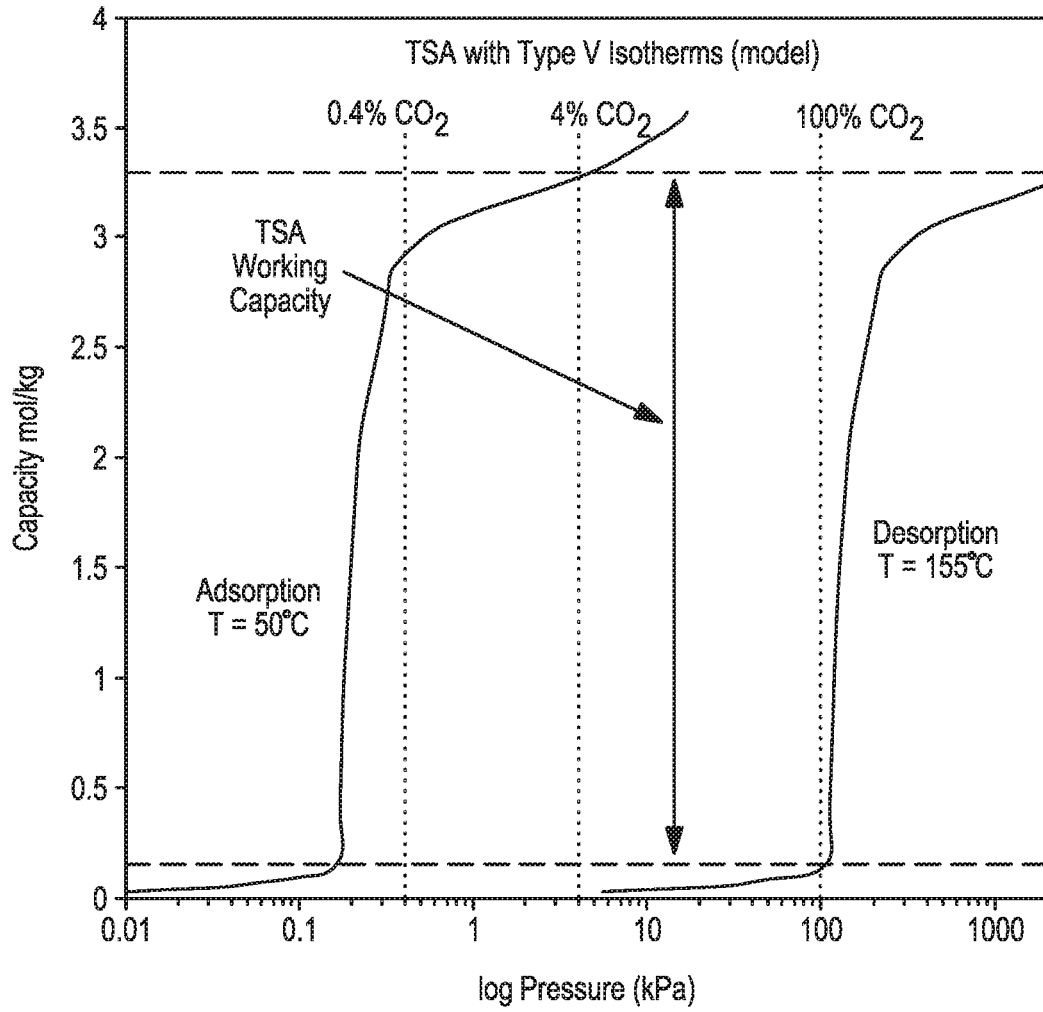


FIG. 3

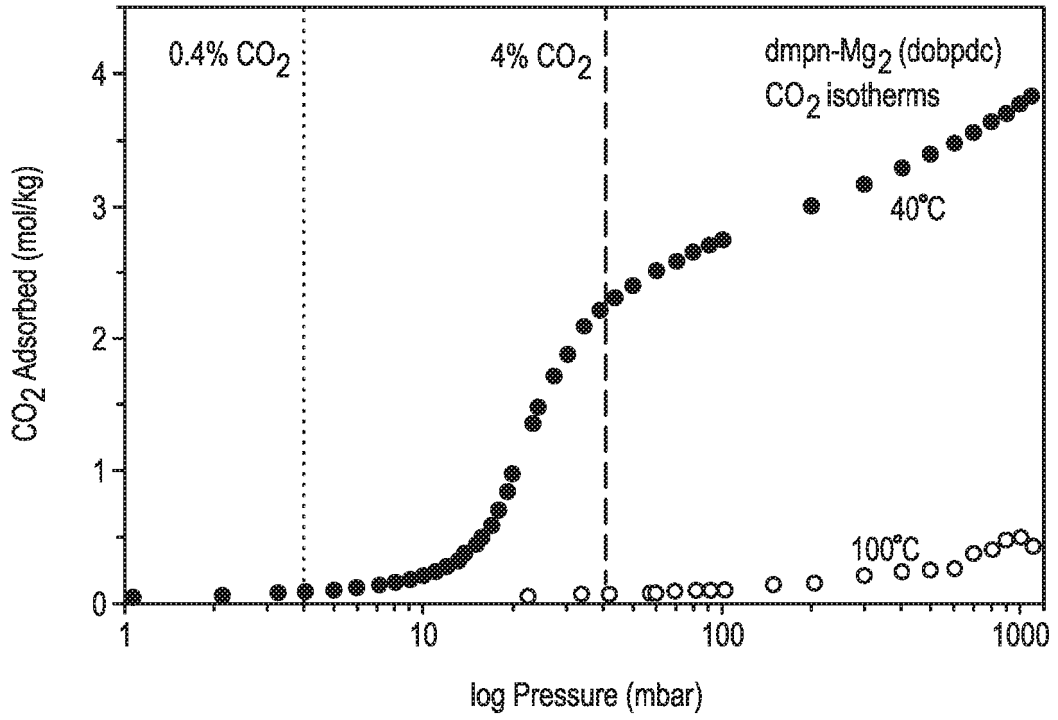


FIG. 4A

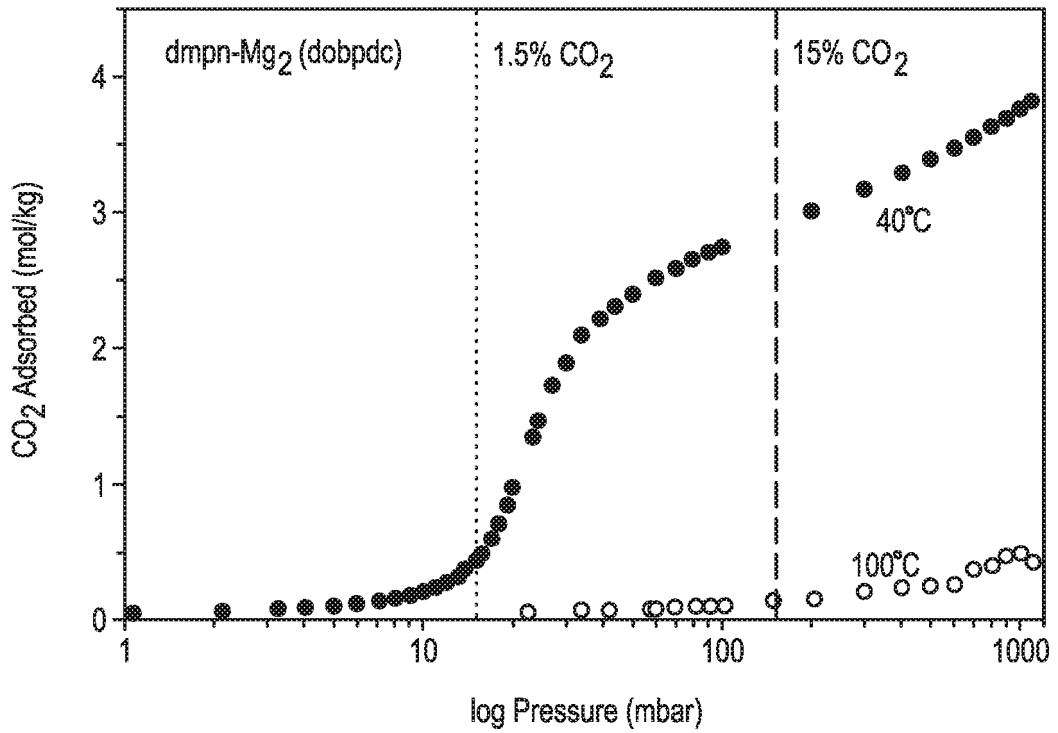


FIG. 4B

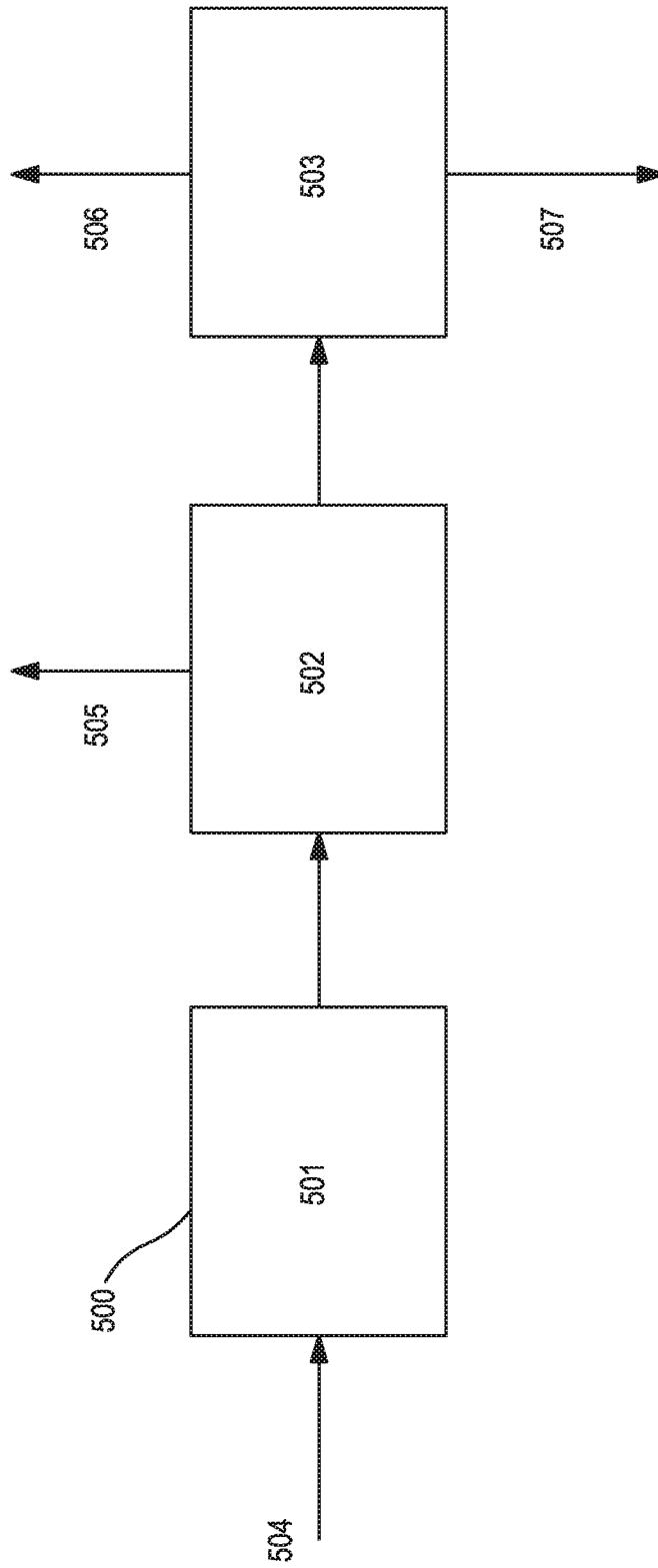


FIG. 5

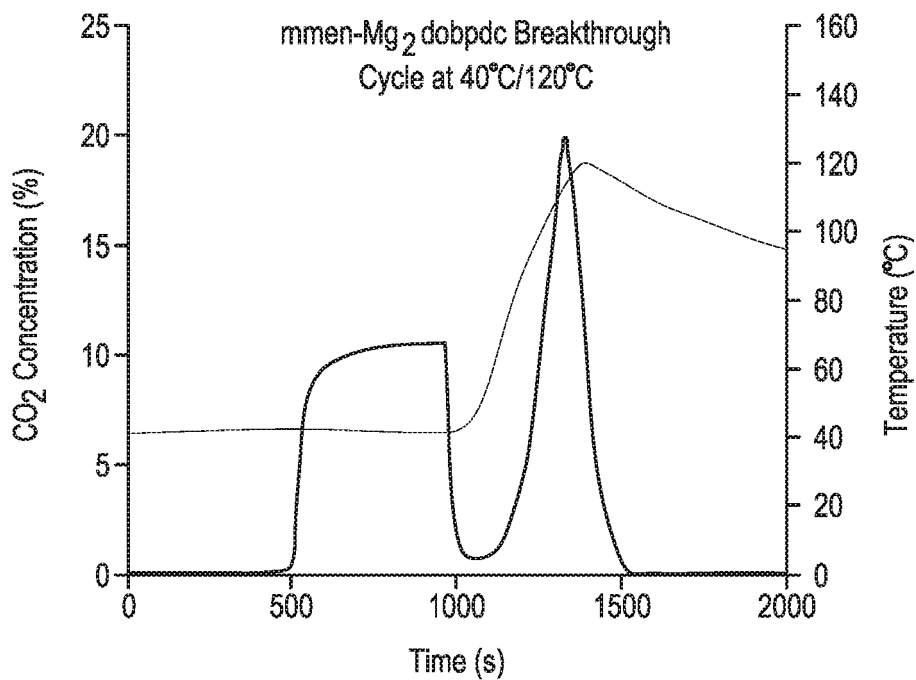


FIG. 6A

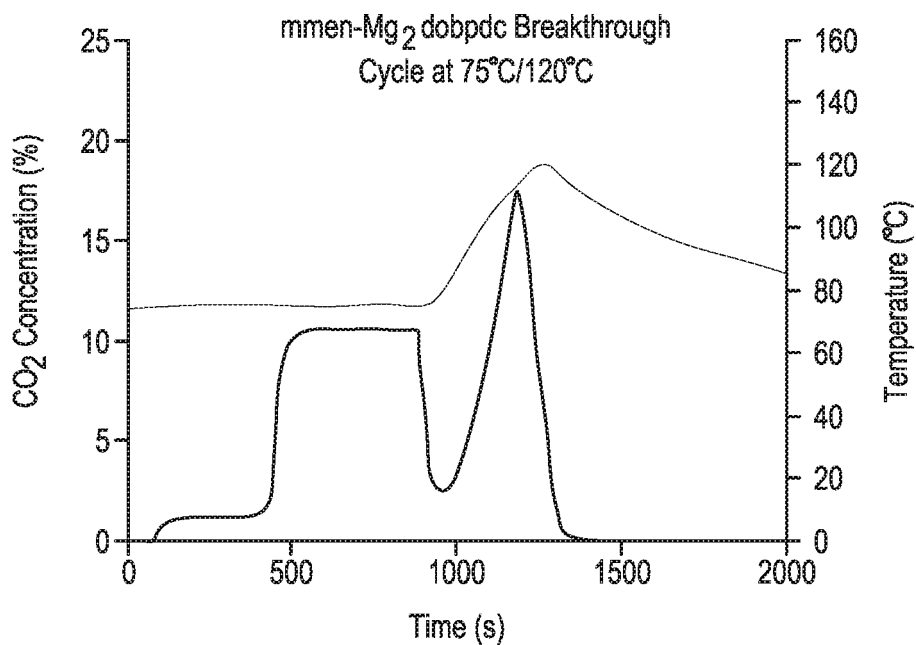


FIG. 6B

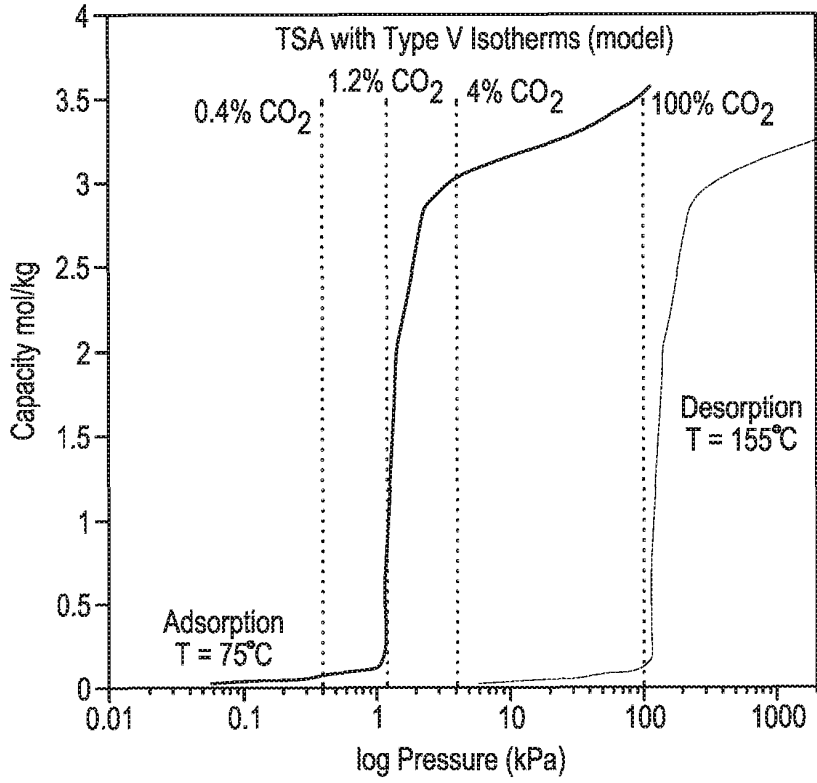


FIG. 7A

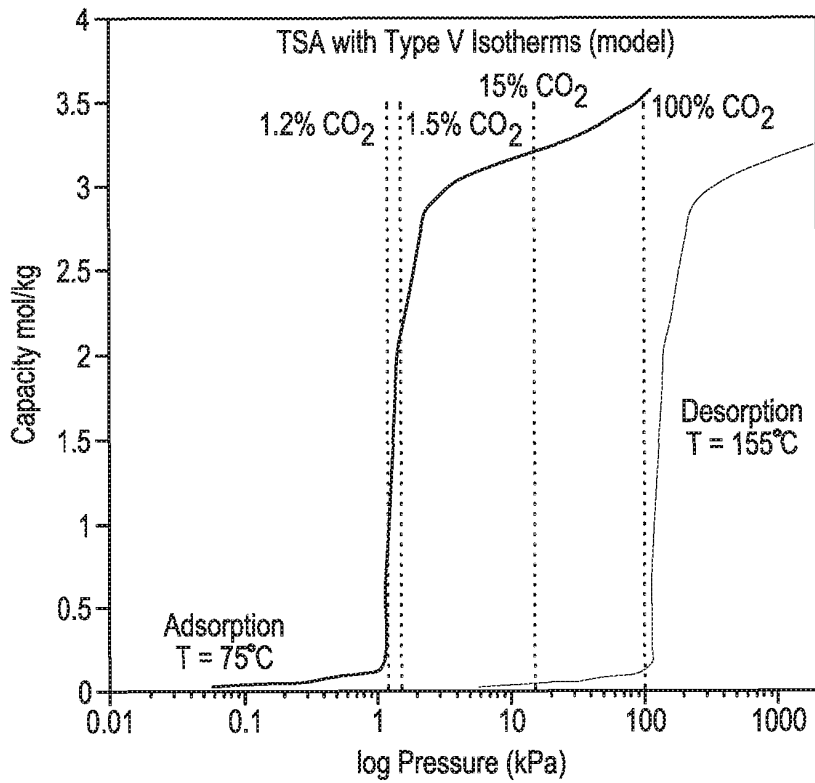


FIG. 7B

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 20170087531 A [0007]
- US 20170087503 A, Sundaram [0031]
- US 20170087506 A [0035]

Non-patent literature cited in the description

- **MCDONALD et al.** *J. Am. Chem. Soc.*, 2012, vol. 134, 7056-7065 [0007]
- **MCDONALE et al.** *Nature*, 2015, vol. 519, 303-308 [0007]
- **THOMAS M. MCDONALD ; WOO RAM LEE ; JARAD A. MASON ; BRIAN M. WIERS ; CHANG SEOP HONG ; JEFFREY R. LONG.** *J. Am. Chem. Soc.*, 2012, vol. 134, 7056-7065 [0028]
- **MILNER, PHILLIP J. et al.** A Diaminopropane-Appended Metal-Organic Framework Enabling Efficient CO₂ Capture from Coal Flue Gas Via a Mixed Adsorption Mechanism. *Journal of the American Chemical Society*, 2017, vol. 139, 13541-13553 [0029]
- **MERKEL, T.C. et al.** Selective Exhaust Gas Recycle with Membranes for CO₂ Capture from Natural Gas Combined Cycle Power Plants. *INDUS. & ENG'G CHEM. RES.*, 2013, vol. 52, 1150-59 [0031]